

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-012860

(43)Date of publication of application : 14.01.1997

(51)Int.Cl.

G08L 71/02

G08K 5/09

G08K 5/17

G08L101/10

(21)Application number : 07-164188

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(22)Date of filing : 29.06.1995

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(54) ROOM-TEMPERATURE-CURABLE COMPOSITION

(57)Abstract:

PURPOSE: To obtain a room-temp.-curable compsn. which exhibits a sufficient depth cure rate and is free from troubles, such as the viscosity increase of the main component, even during long stroage by compounding a specific org. polymer with a cure catalyst, an org. amine compd., and a filler.

CONSTITUTION: This compsn. is prepd. by mixing and kneading 100 pts.wt. org. polymer which is derived from a hydroxylated polyoxyalkylene polymer obtd. by polymerizing an alkylene oxide using an initiator in the presence of a composite metal cyanide complex as the catalyst and has hydrolyzable silicon groups represented the formula (R1 is a 1-20C monovalent hydrocarbon group, R2 is a divalent org. group; X is a hydroxyl or hydrolyzable group; and a is 1-3) and a total content of ionic impurities of 50ppm or lower with 0.01-10 pts.wt. cure catalyst selected from among 20C or lower aliph. carboxylates of divalent tin, divalent bismuth, and divalent lead, 0.01-10 pts.wt. org. amine compd., 50-250wt.% (based on the polymer) filler, and optional plasticizers and additives.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] **Industrial Application** This invention relates to the room-temperature-curing nature constituent hardened under hygroscopic-surface-moisture existence.

[0002] **Description of the Prior Art** The method of using it for a sealing material, adhesives, etc. using the hardening reaction of organic polymers which have a hydroxylic silicon group at the end and which is known as conventional, for example, modified silicone, system resin is known well, and is used in many methods.

[0003] **Problem(s) to be Solved by the Invention** The organic polymer which has a hydroxylic silicon group at the end is solved by JP-46-75533-B, JP-46-75533-B, JP 61-18922-B, etc. for example.

[0004] In order to give room-temperature-curing nature to an end, especially with the organic polymer which has alkoxyl alkyl groups as a hydroxylic silicon group among the organic polymers which have a hydroxylic silicon group, using what is called a curing catalyst is usually performed. As such a curing catalyst, organic metallic compounds, such as metal salt of carboxylic acid, acid, or a basic compound is known, and carboxylate of tin and other organotin compounds are especially common.

[0005] The organic polymer which has a hydroxylic silicon group at the end, various bulking agents, a plasticizer, it is divided roughly into 2 gestalten called what is called a 1 liquid type and a 2 liquid type as a result of the combination when using the resin composition of the room-temperature-curing nature which blends an adhesive grant agent, a thiothropy grant agent, a curing catalyst, various stabilizer, etc. for a sealing material, adhesives, etc.

[0006] What is known as a 2 liquid type among those is divided into base resin and a hardening agent, it mixes colorant etc. with these two ingredients if needed further, constructs, and makes it harden in a service space at the time of use. As for the hardening agent in this 2 liquid type, it is common to include the curing catalyst, and as this curing catalyst, since a hardened material shows good compression restoration nature to a repetition of elasticity, isaken carboxylate or carboxylic acid of a divalent tin and the organic amine compound, the method of specifically using cyclohexyl acid tin and lauryl amine are proposed (refer to JP-61-90873-B).

[0007] However, it is by this method of introducing a hydroxylic silicon group, after a dihalo compound's using the polyether compound of the comparatively short molecular weight proposed by the aforementioned well-known example, setting it and carrying out Polymer Dimerization quantification. If cyclohexyl acid tin and lauryl amine are used as a curing catalyst when the polymer and bulking agent which have a hydroxylic silicon group are used as base resin, by a part far from the surface of a cure rate, especially a cured body, the so-called cure rate of the depths is insufficient, and it cannot be satisfied.

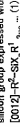
[0008] When the organic polymer containing the hydroxylic silicon group manufactured by the end from the polyoxalene polymer which manufactured as a catalyst the composite metal cyanide complex [given as an organic polymer which has a hydroxylic silicon group] in JP-8-33449-A, JP-8-79827-A is used as base resin, in order not to usually perform strict moisture control (that is, let the amount of [in base resin] water content fall) when manufacturing base resin although the hardenability of the depths improves remarkably if the curing catalyst is used, there was a case

where the viscosity of base resin rose during long-term preservation, and use top inconvenience arose.

[Means for Solving the Problem] This invention is the following invention which is going to cancel such a fault.

[0010] A curing catalyst (B) chosen from the following organic polymer (A), carboxylate of divalent tin, cyclohexyl acid tin, and a complex of divalent lead and an organic amine compound (C) and a temperature-curing nature constituent containing a bulking agent (D).

[0011] [Organic polymer] It is derived from an initiator group content polyoxyalkylene polymer (F) produced by polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex (E) into a catalyst. An organic polymer (A) whose total amount of an ionic impurity it has a hydroxylic silicon group expressed with a formula (1), and is 50 ppm or less.



[0013] As for R¹, a hydroxylic group or a hydroxylic basis, and a of substitution of the carbon numbers 1-20 or a unsubstituted univalent hydrocarbon group, and R² are the integers of 1-3 a divalent organic group and X among a formula.

[0014] [Organic polymer] An organic polymer (A) is derived from a hydroxylic group content polyoxyalkylene polymer (F) produced by polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex (E) into a catalyst.

[0015] By using a composite metal cyanide complex (E), using the conventional alkaline metal catalyst, M_n/M_w is [rather than] small and a hydroxylic group content polyoxyalkylene polymer (F) of hydroviscosity can be obtained more in the amount of Polymer Division.

[0016] A complex which uses zinc hexa cyanocobaltate as the main ingredients as a composite metal cyanide complex (E) is preferred, and the other and/or especially an alcoholic complex are preferred. The presentation can use what is intrinsically indicated to JP-546-27200-B. As ether, ethylene glycol dimethyl ether (glyme), diethylene glycol dimethyl ether (diglyme), etc. are preferred, and especially glyme is preferred from handling at the time of manufacture of a complex. As alcohol, t-butanol is preferred.

[0017] A compound which has 2-10 active hydrogen as an initiator is preferred, a polyhydroxy compound, preferred is polyhydroxy compound which has 2-4 hydroxyl groups especially is preferred. Specifically Ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, neopentyl glycol, 1,4-butanediol. There is a polyol of low molecular weight from an object produced by making alkylene oxide react to 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, diglycerol, a shock resist, and these. One-sirt single use or two or more sorts of compound use may be sufficient as these. An unsaturation group content mono- hydroxy compound like allyl alcohol can also be used.

[0018] A total amount of an ionic impurity of an organic polymer (A) of this invention is 50 ppm or less. This invention is suitable when especially an ionic impurity is an ionic impurity containing metallic compounds and/or an alkali metal compound resulting from a composite metal cyanide complex (E). It is preferred that ionic impurities are 30 ppm or less and 20 ppm or less.

[0019] By reducing such metal impurity quantity, the storage stability of an organic polymer (A) and a hardenability constituent of this invention is improved more, and also hardenability which was excellent in use not to bar an operation of a curing catalyst is acquired.

[0020] Following (D) - a method of (D) are mentioned as the reducing method. Methods of using it when removing metallic compounds resulting from especially a composite metal cyanide complex (E) include (D). Especially since a method can reduce an ionic impurity effectively and economically, it is desirable.

[0021] How to remove this salt from a polymer after making into an infeasible salt intrinsically contained in a part to polymer. After adding the Naion system surface-active agent (soluble salt to a polymer intrinsically, by drying, a salt is deposited and there is a method of next removing this salt. As a compound which can form a salt, chloride, sulfuric acid, nitric acid, phosphoric acid, pyrophosphoric acid, disodium dihydrogen phosphosphate, etc. are preferred. A deposited salt is removable by filtration operation, adsorbing operation, etc.

[0022](ii) How to make an anion exchange resin and/or cation exchange resin contact, and to remove an ionic impurity after adding a solvent to a polymer.

[0023] To a buffer for pH and a britation, by ammonia and a chelating agent (III) After processing, A method of removing metallic compounds which originate in a composite metal cyanide complex (E) after adding a reagent and fatty alcohol from which metallic compounds resulting from a composite metal cyanide complex (E) are removed, and a chelating agent, a method of removing metallic compounds which originate in a composite metal cyanide complex (E) after processing with an

Context: With an ionic impurity as used in the field of this invention, originate in a composite metal cyanide complex (E). A cation and anions, such as zinc ion, cobalt ion, osydate ion, and a chloride ion. Mix as an impurity at a process of manufacturing an organic polymer (A). Sodium ion, alkali metal ion, potassium ion, carboxylate ion that polyoxalates generated in response to oxidation at a process of manufacturing a halogen ion; organicity polymer (A). An organic polymer (A) at a process to manufacture an ester bond. All the anions, such as catalyst metal salt added when making carboxylic acid combination (E) form, and cations are included.

[0025] As for an organic polymer (A), what replaced a hydrogen atom in a hydroxyl group of a hydroxyl group content n-bisoxazulene polymer (F) by a formula (1) is preferred.

[0026] As for the number of hydroxyl groups per molecule of a polyoxalkylene polymer (F) used for the present invention, it is especially preferred that they are 2–10 pieces. It is especially preferred from balance of physical properties, such as viscosity, intensity, and elongation, that they are especially 2–4 pieces or 8 pieces.

[0027] Desirable polymers (F) are polyoxypropylene diol, polyoxypropylene triol, and polyoxypropylene tetraol. When using for a method of the following (b) or (**), unsaturation group end polyoxyalkylene monomers, such as polyoxypropylene glycol monoallyl ether, can also be used.

[0228]As for a hydroxyl value conversion molecular weight of a polyoxalkylene polymer (F), 5000–30000 are preferred, and 8000–30000 are more preferred.

[0229]A hydroxyl value conversion molecular weight of this invention says a thing of a molecular weight calculated by a product of a functional group number of an initiator, and a molecular weight per hydroxyl group of polyoxalkylene of a polymer used when manufacturing a polyoxalkylene polymer (F) containing terminal hydroxyl groups.

[0030] An organic polymer (A) has a hydrolytic silicon group expressed with a formula (1).



[0052] As an organic amine compound (C) of this invention, with a carbon number of 20 or less monoamine or with a carbon number of 20 or less polyamine is preferred. A compound which has a hydrolytic silicon group expressed with an amino group and a formula (2) to intramolecular is preferred.



obtained. The after-manufacture viscosity of the organic polymers SI-S14 is also shown in a table. The content of the methyl dimethyl silyl group as an end group is the range of organic polymer 1g per 0.11mmol ~ 0.17mmol. The amount of residual metal ions of the obtained organic polymers SI-S14 was not different from before methyl dimethyl silyl group introduction. [0070] (Examples 15-23) 60 copies of calcium carbonate, 60 copies of diethyl phthalate, five copies of hydrogenation castor oil, one copy of phenolic antioxidant, 0.5 copy of ultraviolet ray absorbent, and 0.5 copy of light stabilizer were added and kneaded to 100 copies of organic polymers (SI-S14), and kneaded to form a base resin (M1-M14). [0071] On the other hand, 20 copies of calcium carbonate, three copies of lauryl amine, 20 copies of diethyl phthalate, and 60 copies of calcium carbonate were kneaded, and it was considered as the hardening agent (K1-K5). [0072] The viscosity (after-storage viscosity) (unit: cP) after storing for 14 days at the viscosity measured. A result is shown in Table 3-4.

[0073] (Examples 24-45) 100 copies of base resin (M1-M14) and 8.5 copies of hardening agents (K1-K5) [0073] (Examples 24-45) 100 copies of base resin (M1-M14) and 8.5 copies of hardening agents (K1-K5) which were mixed in the table below were kneaded, the hardenability constituent was slushed so that it might become a thickness of 3 cm into the cup of a cylindrical shape 4 cm in diameter, and it was neglected under the atmosphere of 20 °± and 65% humidity for 8 hours. The situation of hardening to a depth direction from the surface was seen using the penetrometer based on JISK-2530 after that. A result is shown in Table 5-7. The one where penetration is larger means that hardening from the surface is not progressing.

[0080] (Purification method A) The polyoxypropylene polymer 5g, the water 50g, and the disodium hydrogen pyrophosphate 10g of the molecular weight 1000 to which 10 % of the weight of ends were made to carry out block polymerization of the ethylene oxide were added to 1 kg of organic polymers which contain metal salt etc. as an impurity, and it agitated at 90 °± for 1 hour. Then, after distilling off water under 90 °± and decompression, after adding 10 g and carrying out decompression drying of the KTO word 000 Synthetic MAGNET-SHM silicate, harmony chemicals company make) at 80 °± for 1 hour, 2 l of hexane was added, the organic polymers were dissolved, and the insoluble matter was removed. The insoluble matter was removed by filtering with filter paper. It distilled off under decompression of hexane after that, and refining things were obtained.

[0081] (Purification method B) 1 kg of organic polymers which contain metal salt etc. as an impurity were dissolved in 3 kg of hexane, 1 kg of sulfuric acid water was added, 3% of the weight, and the whole has become turbid although agitated for 1 hour. Although allowed to stand at the room temperature for three days, since the hexane layer a little transparent [about 1/5] to the top layer dissociated, the hexane layer was divided by the decantation, hexane was distilled off under decompression, and refining things were obtained.

[0082]

[Table 1]

例	1	2	3	4	5	6	7
有機重合体	P1	P2	P3	P4	P5	P6	P7
精製法	ア	ア	ア	ア	ア	ア	ア
精製後粘度	6500	7500	10000	5500	12000	13000	9000
硬化剤イオン濃							
Na ⁺ 濃	1以下	4	2	5	3	3	2
Ca ²⁺ 濃	1以下	1以下	1以下	1以下	1以下	1以下	1以下
Cl ⁻ 濃	1以下	5	3	8	5	5	5
有機重合体S1	S1	S2	S3	S4	S5	S6	S7
硬化後粘度	8300	9000	17000	7500	13000	13500	9500

[0083]

[Table 2]

例	8	9	10	11	12	13	14
有機重合体	P1	P2	P3	P4	P5	P6	P7
精製法	イ	イ	イ	イ	イ	イ	イ
精製後粘度	6500	7500	15000	5500	12000	13000	9000
硬化剤イオン濃							
Na ⁺ 濃	2.5	2.2	3.2	3.5	2.6	3.8	2
Ca ²⁺ 濃	5	3	3	5	4	5	0
Cl ⁻ 濃	2	4	3	3	4	5	0
有機重合体S1	S8	S9	S10	S11	S12	S13	S14
硬化後粘度	9000	10000	19000	8500	12000	10000	9500

[0084]

[Table 3]

例	15	16	17	18	19	20	21
有機重合体	S1	S2	S3	S4	S5	S6	S8
主剤	M1	M2	M3	M4	M5	M6	M7
精製後粘度	1.57	1.67	2.47	1.37	1.77	2.07	1.77
硬化後粘度	1.67	1.57	2.57	1.37	1.87	2.17	3.57

[0085]

[Table 4]

例	22	23	24	25	26	27	28
有機重合体	S9	S10	S11	S12	S13	S7	S14
主剤	M8	M9	M10	M11	M12	M13	M14
精製後粘度	1.87	2.67	1.57	1.97	2.07	1.77	1.77
硬化後粘度	4.57	5.57	3.77	4.07	5.27	1.67	1.87

[0086]

[Table 5]

例	29	30	31	32	33	34
主剤	M1	M2	M3	M4	M5	M6
精製後粘度	K1	K1	K1	K2	K3	K4
粘度	0.7	0.7	0.5	0.8	0.7	0.5

[0087]

[Table 6]

例	35	36	37	38	39	40
主 剤	M7	M8	M9	M10	M11	M12
硬化剤	K1	K1	K1	K2	K3	K4
針入度	0.6	0.6	0.4	0.7	0.5	0.4

[0088]

[Table 7]

例	41	42	43	44	45
主 剤	M7	M14	M1	M2	M3
硬化剤	K1	K1	K5	K5	K5
針入度	1.5	1.5	2.5	2.5	2.1

[0089]

[Table 8]

硬化剤	含有する金属カルボン酸塩
K1	オクチル酸スズ (2価) (日本化学産業製ニッカオクチル酸スズO)
K2	オクチル酸ピスマス (2価) (京都化成社ニッカオクチル酸スズO)
K3	パーオクチル酸ピスマス (2価) (The Shepherd Chemical 社製(SHEPHERD VESCALAB))
K4	ネオパラン酸ピスマス (3価) (The Shepherd Chemical 社製(SHEPHERD VESCALAB))
K5	ジブチルスズジタワレート (4価)

[0090]

Effect of the Invention: Storage stability is improved remarkably and the hardenability constituent of this invention has the good hardenability of the depths.

[Translation done.]

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CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by regulation of Patent Law Article 17 of 2

[Section Type] The 3rd type of the part II gate

[Publication date] Heisei 11 (1999) November 28

[Publication No.] JP-9-2280A

[Date of Publication] Heisei 9 (1997) January 14

[Annual volume number] Publication of patent applications 9-129

[Application number] Japanese Patent Application No. 7-184188

[International Patent Classification (6th Edition)]

008L 71/02 LOC

008K 5/09 KAR

5/17 MAY

008L 03/10

[F]

008L 71/02 LOC

008K 5/09 KAR

5/17 MAY

[Written Amendment]

[Filing date] Heisei 11 (1999) March 10

[Amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claims

[Method of Amendment] Change

[Proposed Amendment]

[Claim(s)]

[Claim 1A] curing catalyst (B), chosen from the following organic polymer (A), carboxylate of divalent tin, carboxylate of divalent bismuth, and carboxylate of divalent lead, and an organic amine compound and a room-temperature-curing nature constituent containing a bulking agent (D).
[Organic polymer (A)] It is derived from a hydroxyl group content polyoxaalkylene polymer (F) produced by polymerizing alkylene oxides in an initiator by making a composite metal cyanide complex (E) into a catalyst. An organic polymer (A) whose total amount of an ionic impurity it has a hydrolytic silicon group expressed with a formula (1), and is 50 ppm or less.

$-R^1-SiX_3-R^2$ (1)

As for R^1 , a hydroxyl group or a hydrolytic basis, and a of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and R^2 are the integers of 1-3 a divalent organic group

and X among a formula

[Claim 2] The room-temperature-curing nature constituent according to claim 1 whose organic amine compound (C) is a compound which has at least one of 20 or less amine or a hydrolytic silicon group expressed with an amino group and a formula (2) to nonmolecular.

$-R^3-SiX_3-R^4$ (2)

As for a divalent organic group and R^1 , a hydroxyl group or a hydrolytic basis, and b of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X^1 are [R^5] the integers of 1-3 among a formula.

[Claim 3] The room-temperature-curing nature constituent according to claim 1 or 2 which is an ionic impurity in which an ionic impurity contains metallic compounds and/or an alkali metal compound resulting from a composite metal cyanide complex (E).

[Claim 4] An organic polymer (A) an ionic impurity contained in a polymer (F). After an ionic impurity contained in a polymer (F) by removing this salt from a polymer (F) after considering it to a polymer (F) as an insoluble salt intrinsically shall be 50 ppm or less. The room-temperature-curing nature constituent according to any one of claims 1 to 3 which is an organic polymer produced by introducing a hydrolytic silicon group into a polymer (F).

[Claim 5] An organic polymer (A) an ionic impurity contained in a terminal unsaturated group introduction thing (G) of a polymer (F). After an ionic impurity contained in a terminal unsaturated group introduction thing (G) by removing this salt from a terminal unsaturated group introduction thing (G) shall be 50 ppm or less. The room-temperature-curing nature constituent according to any one of claims 1 to 3 which is an organic polymer obtained by making it react to a silicon hydride compound expressed with a terminal unsaturated group introduction thing (G) and a formula (3).

$H-SiX_3-R^1-R^2$ (3)

A hydroxyl group or a hydrolytic basis, and a of R^1 are the integers of 1-3 among a formula substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X

[Claim 6] The room-temperature-curing nature constituent according to any one of claims 1 to 5 whose hydrolytic value conversion molecular weights of a polymer (F) are 5000-30000.

[Translation done.]